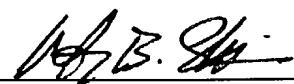


FORM PTO-1390 (REV. 9-95)	U. S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371			ATOCM 249
INTERNATIONAL APPLICATION NO	INTERNATIONAL FILING DATE		U. S. APPLICATION NO (If known, see 37 CFR §1.5)
PCT/FR00/02265	7 AUGUST 2000		10/049377
PRIORITY DATE CLAIMED			
12 AUGUST 1999			
TITLE OF INVENTION			
DETERGENT BIODEGRADABLE POLYACRYLATES			
APPLICANT(S) FOR DO/EO/US			
GANCET, Christian, et al.			
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. §371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. §371. 3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. §371(c)(2)) <ul style="list-style-type: none"> a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. §371(c)(2)). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3)) <ul style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. §371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)). 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)). <p>Items 11. to 16. below concern document(s) or information included:</p> <ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 C.F.R. §§1.97 and 1.98. 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. §§3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <ul style="list-style-type: none"> <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input type="checkbox"/> Other items or information: 			

U.S. APPLICATION NO. (if known; see 37 CFR 1.15)		INTERNATIONAL APPLICATION NO	ATTORNEY'S DOCKET NUMBER																						
107049377		PCT/FR00/02265	ATOCM 249																						
<p>17. <input checked="" type="checkbox"/> The following fees are submitted:</p> <p>BASIC NATIONAL FEE (37 CFR §1.492 (a) (1) - (5)): </p> <table> <tr> <td>Search Report has been prepared by the EPO or JPO.....</td> <td>\$890.00</td> </tr> <tr> <td>International preliminary examination fee paid to USPTO (37 CFR §1.482).....</td> <td>\$710.00</td> </tr> <tr> <td>No international preliminary examination fee paid to USPTO (37 CFR §1.482) but international search fee paid to USPTO (37 CFR §1.445(a)(2)).....</td> <td>\$740.00</td> </tr> <tr> <td>Neither international preliminary examination fee (37 CFR §1.482) nor international search fee (37 CFR §1.445(a)(2)) paid to USPTO.....</td> <td>\$1040.00</td> </tr> <tr> <td>International preliminary examination fee paid to USPTO (37 CFR §1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)</td> <td>\$100.00</td> </tr> </table> <p align="center">ENTER APPROPRIATE BASIC FEE AMOUNT =</p> <p align="right">\$890.00</p>				Search Report has been prepared by the EPO or JPO.....	\$890.00	International preliminary examination fee paid to USPTO (37 CFR §1.482).....	\$710.00	No international preliminary examination fee paid to USPTO (37 CFR §1.482) but international search fee paid to USPTO (37 CFR §1.445(a)(2)).....	\$740.00	Neither international preliminary examination fee (37 CFR §1.482) nor international search fee (37 CFR §1.445(a)(2)) paid to USPTO.....	\$1040.00	International preliminary examination fee paid to USPTO (37 CFR §1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)	\$100.00	CALCULATIONS	PTO USE ONLY										
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<p>Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 C.F.R. §1.492(e)).</p> <table> <tr> <td><input type="checkbox"/> 20</td> <td><input type="checkbox"/> 30</td> </tr> </table>				<input type="checkbox"/> 20	<input type="checkbox"/> 30																				
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<table border="1"> <thead> <tr> <th>CLAIMS</th> <th>NUMBER FILED</th> <th>NUMBER EXTRA</th> <th>RATE</th> </tr> </thead> <tbody> <tr> <td>Total claims</td> <td>11 - 20 =</td> <td>0</td> <td>x \$ 18.00</td> </tr> <tr> <td>Independent claims</td> <td>1 - 3 =</td> <td>0</td> <td>x \$ 84.00</td> </tr> <tr> <td colspan="2">MULTIPLE DEPENDENT CLAIM(S) (if applicable)</td> <td></td> <td>+ \$ 280.00</td> </tr> <tr> <td colspan="4"> TOTAL OF ABOVE CALCULATIONS = </td> </tr> </tbody> </table>				CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	Total claims	11 - 20 =	0	x \$ 18.00	Independent claims	1 - 3 =	0	x \$ 84.00	MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$ 280.00	TOTAL OF ABOVE CALCULATIONS =				\$890.00	
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<p>Reduction of 1/2 for filing by small entity, if applicable. A Verified Small Entity Statement must also be</p>				SUBTOTAL =	\$890.00																				
<p>Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 C.F.R. §1.492(f)).</p> <table> <tr> <td><input type="checkbox"/> 20</td> <td><input type="checkbox"/> 30</td> </tr> </table>				<input type="checkbox"/> 20	<input type="checkbox"/> 30	TOTAL NATIONAL FEE =	\$890.00																		
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<p>Fee for recording the enclosed assignment (37 C.F.R. §1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. §§3.28, 3.31). \$40.00 per property.</p>				TOTAL FEES ENCLOSED =	\$890.00																				
				Amount to be refunded:																					
				charged.																					
<p>a. <input checked="" type="checkbox"/> A check in the amount of <u>\$890.00</u> to cover the above fees is enclosed.</p> <p>b. <input type="checkbox"/> Please charge my Deposit Account No. <u>13-3402</u> in the amount of <u>\$</u> to cover the above fees. A duplicate copy of this sheet is enclosed.</p> <p>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>13-3402</u>. A duplicate copy of this sheet is enclosed.</p>																									
<p>NOTE: Where an appropriate time limit under 37 C.F.R. §§1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. §1.137(a) or (b)) must be filed and granted to restore the application to pending status.</p>																									
SEND ALL CORRESPONDENCE TO: Customer Number 23,599																									
 <u>23599</u> PATENT TRADEMARK OFFICE																									
<p>Filed: 12 FEBRUARY 2002 HBS:kmo</p> <p> SIGNATURE <u>Harry B. Shubin</u> NAME <u>32,004</u> REGISTRATION NUMBER </p>																									

IN THE UNITED STATES DESIGNATED/ELECTED OFFICE

International Application No. : PCT/FR00/02265
International Filing Date : 7 AUGUST 2000
Priority Date(s) Claimed : 12 AUGUST 1999
Applicant(s) (DO/EO/US) : GANCET, Christian, et al.

Title: DETERGENT BIODEGRADABLE POLYACRYLATES

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

SIR:

Prior to calculating the national fee, and prior to examination in the National Phase of the above-identified International application, please amend as follows:

IN THE CLAIMS:

3. (Amended) The hydrophilic polymer as claimed in claim 1, characterized in that the polyacrylic chains are acrylic acid homopolymers with a degree of polymerization of less than or equal to 20.

4. (Amended) The hydrophilic polymer as claimed in claim 1, characterized in that the polyacrylic chains are copolymers of acrylic acid and of other monomers, such as unsaturated carboxylic monomers, maleic anhydride, vinyl or acrylic monomers, or diene monomers, such as isoprene or butadiene, with a degree of polymerization of less than or equal to 20.

5. (Amended) The hydrophilic polymer as claimed in claim 1, characterized in that the connection (X) between the molecule comprising a labile bond and the polycarboxylic chain is composed of a sulfur atom.

6. (Amended) The hydrophilic polymer as claimed in claim 1, characterized in that the labile bond hydrolyzable by the alkaline or enzymatic route, such as an ester, amide, thioester or thioamide bond, or cleavable by chemical or biological oxidation, such as a double or triple bond.

7. (Amended) The hydrophilic polymer as claimed in claim 1, constructed on pentaerythritol tetramercaptopropionate.

8. (Amended) The hydrophilic polymer as claimed in claim 1, constructed on trimethylolpropane trimercaptoacetate.

9. (Amended) The hydrophilic polymer as claimed in claim 1, constructed on glycol dimercaptoacetate.

10. (Amended) Use of the hydrophilic polymer as claimed in claim 1 in compositions for detergency.

11. (Amended) The hydrophilic polymer as claimed in claim 1, characterized in that it is crosslinked by difunctional agents to form carboxylic polymers which can be used as superabsorbants.

REMARKS

The purpose of this Preliminary Amendment is to eliminate multiple dependent claims in order to avoid the additional fee. Applicants reserve the right to reintroduce claims to canceled combined subject matter.

Attached hereto is a marked-up version of the changes made to the claims by the current amendment. The attached pages are captioned "**Version With Markings to Show Changes Made**".

Respectfully submitted,



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AJZ:kmo

Filed: 12 February 2002

VERSION WITH MARKINGS TO SHOW CHANGES MADE

Claims 3 - 11 have been amended as follows:

3. (Amended) The hydrophilic polymer as claimed in claim 1-~~or 2~~, characterized in that the polyacrylic chains are acrylic acid homopolymers with a degree of polymerization of less than or equal to 20.
4. (Amended) The hydrophilic polymer as claimed in claim 1-~~or 2~~, characterized in that the polyacrylic chains are copolymers of acrylic acid and of other monomers, such as unsaturated carboxylic monomers, maleic anhydride, vinyl or acrylic monomers, or diene monomers, such as isoprene or butadiene, with a degree of polymerization of less than or equal to 20.
5. (Amended) The hydrophilic polymer as claimed in ~~any one of the preceding claims 1,~~ characterized in that the connection (X) between the molecule comprising a labile bond and the polycarboxylic chain is composed of a sulfur atom.
6. (Amended) The hydrophilic polymer as claimed in ~~any one of the preceding claims 1,~~ characterized in that the labile bond hydrolyzable by the alkaline or enzymatic route, such as an ester, amide, thioester or thioamide bond, or cleavable by chemical or biological oxidation, such as a double or triple bond.
7. (Amended) The hydrophilic polymer as claimed in ~~any one of the preceding claims 1,~~ constructed on pentaerythritol tetramercaptopropionate.
8. (Amended) The hydrophilic polymer as claimed in ~~any one of claims 1 to 6,~~ constructed on trimethylolpropane trimercaptoacetate.
9. (Amended) The hydrophilic polymer as claimed in ~~any one of claims 1 to 6,~~ constructed on glycol dimercaptoacetate.

10. (Amended) Use of the hydrophilic polymer as claimed in one of claims 1 to 9 in compositions for detergency.

11. (Amended) The hydrophilic polymer as claimed in one of claims 1 to 9, characterized in that it is crosslinked by difunctional agents to form carboxylic polymers which can be used as superabsorbants.

WO 01/12683

PCT/FR00/02265

BIODEGRADABLE POLYACRYLATES FOR DETERGENCY

The invention relates to the field of detergency and in particular to biodegradable detergent compositions. It 5 discloses more particularly biodegradable polymers comprising polyacrylate-based branches.

Generally, detergent compositions involve a number of chemicals. These must be biodegradable in order not to 10 be harmful to the environment. Conventionally, detergent compositions and cleaning agents include phosphates. The latter are very efficient and relatively nontoxic; however, they lead to the eutrophication of natural aquatic environments.

15 Phosphates have been partially replaced in formulations for detergency by polymers, such as poly(acrylic acid)s or copolymers based on acrylic acid and on maleic anhydride.

20 Although the polyacrylates currently used do not present this problem, their absence of rapid biodegradability leads to an accumulation in the natural environment (Swift, Polymer Degradation and 25 Stability, 45, 215-231, 1994).

Toxicity associated a priori with these polymers is not known but their long-term effect is uncertain and this 30 uncertainty has contributed to the initiation of numerous research studies intended to improve their biodegradability.

It is clearly established that hydrophilic polymers, such as poly(vinyl alcohol), are rapidly degraded by 35 microorganisms (Macromol. Chem. Phys., 196, 3437, 1995). It is also known that poly(acrylic acid)s with a weight-average mass of less than 1 000 exhibit better biodegradability than their higher homologs (Swift,

Ecological Assessment of Polymer, 15, 291-306, 1997).

EP 0 497 611 discloses the preparation of biodegradable terpolymers and of the compositions comprising them.
5 These terpolymers are based on vinyl acetate, acrylic acid and maleic anhydride. They exhibit weight-average masses of less than 20 000.

US 5 318 719 discloses a novel class of biodegradable
10 materials based on the grafting of polymers comprising acid functional groups to a polyoxyalkylene-based biodegradable support.

Other studies indicate that chains comprising
15 heteroatoms are more easily degraded than carbonaceous chains. Thus, US 4 923 941 discloses biodegradable copolymers comprising carboxylic acid functional groups and heterocycles, and the detergent compositions comprising them.

20 The Applicant Company has now found an effective solution for the preparation of biodegradable polymers for detergency.

25 These biodegradable polymers, constituting one of the subject matters of the invention, are composed of hydrophilic acrylic polymers carrying carboxyl functional groups, the structure of which is characterized by a biodegradable core (A) to which are
30 attached at least two polycarboxylic chains (B) via bonds (C) degradable by hydrolysis or by oxidative cleavage. These polymers are also characterized in that each polycarboxylic chain has a degree of polymerization which confers good biodegradability on
35 it and which confers, on the combination, good functional properties with respect to the detergent composition.

These structures thus play their role of builder

throughout a detergency cycle but, because of the high pH of the detergent medium, gradually undergo alkaline hydrolysis of their hydrolyzable functional groups (C), which releases the acrylic polymers (B). The optionally unhydrolyzed residual part will undergo, in a second step, enzymatic hydrolysis by bacterial proteases or esterases active in the natural environment. Finally, only the core, which is readily biodegradable, and the polymers (B), the low molecular mass of which will allow rapid degradability, will remain.

The polymers of the invention correspond to the following general structure:

Core (A) - [-cleavable bond (C) -X-hydrophilic acrylic polymer (B)]_n

in which n is an integer between 2 and 10 and X is a bivalent atom, such as sulfur.

The core A according to the invention is generally a branched biodegradable molecule or a biodegradable molecule which can give rise to at least two branchings chosen from the group comprising pentaerythritol, trimethylolpropane and ethylene glycol.

The polymer B is either a poly(acrylic acid) or a polymer comprising acrylic acid and at least one monomer chosen from the group comprising: unsaturated carboxylic monomers other than acrylic acid, maleic anhydride, vinyl or acrylic monomers, or diene monomers, such as isoprene or butadiene.

B generally has a weight-average mass of between 100 and 2 000.

The functional group C bonding the polymer B to the biodegradable core is a labile bond hydrolyzable by the alkaline or enzymatic route, such as an ester, amide, thioester or thioamide bond, or cleavable by chemical

or biological oxidation, such as a double or triple bond.

5 The biodegradable polymers of the invention can be prepared in various ways. They are advantageously prepared in the following way:

In a first step, the B-X block is prepared, taking care to terminate it with a reactive functional group, by 10 radical polymerization of the monomer(s) in the presence of a reactive transfer agent, in this instance a mercaptan. Subsequently, the functionalized block is reacted with the core A. The respective amounts of A and B are defined so as to have the number 15 of desired branches.

Another alternative form of synthesis consists, in a first step, in modifying the core, so as to prepare:

20 Core (A)-(-C-X)_n

and subsequently in polymerizing the monomer(s), so as to directly form the polymer B on the biodegradable core.

25 The examples described later fully illustrate the method of preparation of the biodegradable polymers of the invention.

30 The biodegradability of the polymers prepared is evaluated in the following way:

Evaluation of the degradability and the properties of the polymers

35 The level of degradation obtained is evaluated by liquid chromatography under the following conditions:

Column : TSK 3000 Tosohas

Eluent : 0.1M H₃CCOONa
Flow rate : 0.5 ml/min
Injection : 25 µl after filtration at 0.22 µ
Detection : Differential refractometer
5 Data acquisition : Peaknet Dionex

Calibration of the column is carried out by virtue of polyacrylate standards (Polymer Laboratories).

10 The degradability of the polymer under the conditions of the test is measured by the shift in the peak observed by liquid chromatography toward lower molecular masses.

15 This shift is quantified through a degradability index I₁₀₀₀ defined in the following way:

- Initial mass of the polymer : M_i
- Final mass of the polymer : M_f
20 - Numbers of cleavages : n_c = $\frac{M_i}{M_f} - 1$
- Initial degree of polymerization : d_p = $\frac{M_i}{M_{\text{mono}}}$
- with M_{mono} : mass of the "average" monomer
- Degradability index : I₁₀₀₀ = $\frac{n_c}{d_p} \times 1000$

25 i.e.: I₁₀₀₀ = $(\frac{M_i}{M_f} - 1) \times \frac{M_{\text{mono}}}{M_i} \times 1000$

1 - Alkaline degradation

30 The sample of polymer is dissolved in a 0.08M borate buffer, pH 12, in a proportion of 10 mg of polymer per 10 ml of buffer solution. Each trial is subsequently stirred magnetically for a predetermined time in a bath thermostatically controlled at the desired temperature.

Analysis is carried out by liquid chromatography (see above) directly on a withdrawn sample of the reaction mixture after neutralization with 0.1M HCl, in a proportion of 1 ml of HCl per 1 ml of withdrawn sample.

5

2 - Microbiological degradation

Respiration test: Warburg method

10 The respiration of *C. tropicalis* on a polyacrylate is evaluated in Warburg flasks (total capacity 3 ml) comprising 1.3 ml of 0.1M phosphate buffer, pH 6, 1 ml of yeast suspension (approximately 3 mg dry weight) and 0.5 ml of 1.12 g.l⁻¹ polyacrylate (final concentration 15 of 200 ppm).

Control tests are carried out in parallel:

- a flask comprising only phosphate buffer (2.8 ml) makes it possible to measure the variations in atmospheric pressure,
- the endogenous respiration is measured in a flask comprising only phosphate buffer (1.8 ml) and the yeast suspension (1 ml),
- the respiration due to contaminants possibly present in the acrylate solution is also evaluated by a test comprising the acrylate (0.5 ml) and the phosphate buffer (2.3 ml),
- the flasks are agitated in a water bath at 30°C,
- the measurements of variation in pressure due to the appearance of CO₂, which reveals metabolism of the acrylate by the yeast, are made every 15 minutes.

Assimilation test: cultures of complex flora on polyacrylate

35

These cultures are employed on a conventional mineral medium (MgSO₄·7H₂O 3 g; CaCl₂·2H₂O 0.1 g; NaCl 1 g; FeSO₄·7H₂O 0.1 g; ZnSO₄·7H₂O 0.1 g; CoCl₂ 0.1 g; CuSO₄·5H₂O 10 mg; AlK(SO₄)₂·12H₂O 10 mg; H₃BO₃ 10 mg;

Na₂MoO₄·2H₂O 2 mg; q.s. for 1 liter of distilled water) in combination with 0.1M phosphate buffer, pH 7, in the proportions 2/98. The polyacrylate tested is at a final concentration of 500 ppm.

5

The treatment plant sludges* are diluted to a third in 0.1M phosphate buffer, pH 7, with 100 mg.l⁻¹ of sample of polyacrylate to be tested, and then the culture is subcultured on a medium comprising 500 mg.l⁻¹ of 10 polyacrylate to be tested. The flasks are incubated at 30°C in Monod tubes with transverse agitation and are subcultured after one week. The culturings are then continued for 30 days under the same conditions.

* Treatment plant at Trefts, Var, France.

15

3 - Evaluation of the ability to complex calcium

The principle of this test consists in measuring the ability of a given polymer to prevent the formation of 20 a CaSO₄ precipitate from sodium sulfate and calcium chloride.

The following examples illustrate the invention without limiting it.

25

- Examples

1 - Synthesis of the polytelomers in the solvent phase

30 50 ml of THF (tetrahydrofuran), acrylic acid, a multifunctional transfer agent and AIBN (azobisisobutyronitrile) are introduced into a 100 ml two-necked round-bottomed flask equipped with a reflux condenser and a nitrogen inlet.

35

The reaction mixture is degassed by a succession of vacuum and nitrogen cycles and then placed in an oil bath thermostatically controlled at 70°C. The polymerization takes place under batchwise conditions

at reflux of the solvent (THF). After reacting for 12 hours, the reaction mixtures are concentrated on a rotary evaporator and then the residues are precipitated from ethyl ether, filtered off (sintered 5 glass filter No. 5) and dried in an oven under vacuum (5×10^{-2} bar) for a minimum of 6 hours.

The natures and the amounts of the reactants are specified in the table below:

10

Reference	Amount acrylic ac., g	Transfer agent	Amount transfer agent, g	Amount AIBN, g	M _n
BG104	11.52	4RSH	2.44	0.27	2 876
BG106	5.76	4RSH	2.44	0.13	1 459
CL17	5	2RSH	0.46	0.11	1 841
CL19	5	4RSH	1.08	0.12	2 187
CL35	5	3RSH	1.03	0.23	1 733

4RSH = PETTMAP = pentaerythritol tetrakis(3-mercaptopropionate)

15 3RSH = TMPTMA = trimethylolpropane tris(2-mercaptopacetate)

2RSH = EGBTG = ethylene glycol bismercaptoacetate

The structures obtained are as follows:

Reference	Number of branches	Structure	n
BG104	4	$\text{---C---}(\text{CH}_2\text{OCOCH}_2\text{CH}_2\text{S}(\text{CH}_2\text{CHCOOH})_n\text{H})_4$	8
BG106	4	$\text{---C---}(\text{CH}_2\text{OCOCH}_2\text{CH}_2\text{S}(\text{CH}_2\text{CHCOOH})_n\text{H})_4$	4
CL19	4	$\text{---C---}(\text{CH}_2\text{OCOCH}_2\text{CH}_2\text{S}(\text{CH}_2\text{CHCOOH})_n\text{H})_4$	5
CL17	2	$\text{---}(\text{CH}_2\text{OCOCH}_2\text{S}(\text{CH}_2\text{CHCOOH})_{20}\text{H})_2$	-
CL35	3	$\begin{array}{c} \text{CH}_2\text{CH}_3 \\ \\ \text{---C---}(\text{CH}_2\text{OCOCH}_2\text{S}(\text{CH}_2\text{CHCOOH})_{10})_3 \end{array}$	-

BG104, BG106 and CL19 are constructed on penta-
erythritol tetramercaptopropionate.

CL17 is constructed on glycol dimercaptoacetate.

5

CL35 is constructed on trimethylolpropane trimercapto-
acetate.

2 - Alkaline degradation of the polymers

10

Alkaline hydrolysis: pH 12, 40°C

Sample	M _i (at t = 0)	M _f (at t = 120 min)
BG 104	3 180	1 400
CL17	1 850	1 600
CL19	1 980	1 350
CL35	1 570	1 350

Alkaline hydrolysis: pH 12, 60°C

15

Sample	M _i (at t = 0)	M _f (at t = 180 min)
BG 104	3 180	1 300
CL17	1 850	1 500
CL19	1 980	1 300
CL35	1 570	1 360

These results indicate that there is clearly a decrease
in the molecular mass under the effect of alkaline
hydrolysis, in particular for the polytelomer BG104.

20

3 - Microbiological degradation

The polytelomer BG104 was evaluated by microbiological
degradation under the conditions described above. Two
25 types of results were obtained:

a - *Respiration test (Warburg method)*

The polytelomer BG104 was furthermore used as carbonaceous substrate for cultures of *Candida tropicalis* in comparison with easily metabolized control glucose and with a reference polyacrylate.

5

The respiration values are as follows:

Substrate	Nature	Respiration μl O ₂ /h.mg of cells
Glucose	-	17.3
BG104	see above	3.1
Norasol 4500	acrylic ac. Homopolymer	0

10 In comparison with a standard polyacrylate, which does not result in any respiration, the polytelomer BG104 exhibits a specific respiration rate approximately 18% that of glucose, which indicates a marked increase in the biodegradability.

15 *B - Assimilation test*

20 The polytelomer BG104 was used as carbonaceous substrate for cultures of microorganisms resulting from treatment plant sludges and was analyzed by comparative liquid chromatography after culturing for 15 days.

25 Analysis of the results indicates that 27% of the polytelomer was degraded by the complex flora present in the culture medium. Washing the biomass with a suitable saline solution did not reveal any trace of polymer, evidence that there has indeed been degradation and not simple adsorption of the polymer.

30 4 - Ability to complex calcium

Two aqueous solutions are prepared from distilled water to comprise the following salts:

Solution A: CaCl₂·2H₂O 64.9 g/l + MgCl₂ 0.5 g/l

Solution B: Na_2SO_4 62.7 g/l

400 ml of distilled water are introduced into a 500 ml flask, followed by the gradual addition of 50 ml of solution A, with stirring, and subsequently by the addition of 50 ml of solution B. Nothing more is added to a flask acting as control, whereas a certain amount of antitartar agent is added to the other flasks. At time $t = 0$, after homogenization of the solutions, a few ml of solution are withdrawn and the calcium and the magnesium therein are quantitatively determined. The flasks are stoppered and then left standing for 7 days. A few ml of supernatant liquor are then withdrawn and the calcium and the magnesium are again quantitatively determined.

The concentration of the ions is measured by emission spectrometry with the help of the ICP (Inductively Coupled Plasma) technique.

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Table of results:

Ref.	ppm	Content of Ca^{2+} in ppm at $t = 0$	Content of Ca^{2+} in ppm at $t = 7$ days
BG104	0.1	1 650	1 050
	0.2	1 620	1 560
	0.4	1 600	1 510
BG106	0.1	1 680	990
	0.2	1 650	1 290
	0.4	1 640	1 610
CL17	0.1	1 550	1 450
	0.2	1 600	1 650
	0.4	1 650	1 700
CL19	0.1	1 500	1 400
	0.2	1 600	1 650
	0.4	1 600	1 650
CL35	0.1	1 700	1 350
	0.2	1 650	1 650
	0.4	1 600	1 650
Norasol 4500	0.1	1 660	960
	0.2	1 640	1 450

	0.4	1 670	1 630
Control		1 660	900

Interpretation:

At 0.1 ppm of polyacrylate, all the compounds are
5 better than the reference compound, with the following
classification:

Norasol 4500 < BG106 < BG104 < CL35 < CL19 < CL17

10 At 0.2 ppm of polyacrylate, all the compounds except
BG106 are better than the reference compound, with the following
classification:

BG106 < Norasol 4500 < BG104 < CL35 = CL19 = CL17

15 At 0.4 ppm of polyacrylate, all the compounds,
including the reference compound, completely inhibit
the formation of CaSO₄, except BG106, with the following
classification:

20 BG106 < Norasol 4500 = BG104 = CL35 = CL19 = CL17

CLAIMS

1. A hydrophilic polycarboxylic polymer with improved degradability corresponding to the following general structure:

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CORE (A) - [-LABILE BOND (C) -X-POLYCARBOXYLIC CHAIN (B)]_n

10 composed of a biodegradable core (A) to which are attached polycarboxylic chains (B) via bonds (C) easily degradable by alkaline or enzymatic hydrolysis or by oxidative cleavage, X is a transfer agent.

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2. The hydrophilic polymer as claimed in claim 1, characterized in that the number of branches n is between 2 and 10.

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3. The hydrophilic polymer as claimed in claim 1 or 2, characterized in that the polyacrylic chains are acrylic acid homopolymers with a degree of polymerization of less than or equal to 20.

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4. The hydrophilic polymer as claimed in claim 1 or 2, characterized in that the polyacrylic chains are copolymers of acrylic acid and of other monomers, such as unsaturated carboxylic monomers, maleic anhydride, vinyl or acrylic monomers, or diene monomers, such as isoprene or butadiene, with a degree of polymerization of less than or equal to 20.

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5. The hydrophilic polymer as claimed in any one of the preceding claims, characterized in that the connection (X) between the molecule comprising a labile bond and the polycarboxylic chain is composed of a sulfur atom.

6. The hydrophilic polymer as claimed in any one of the preceding claims, characterized in that the labile bond is a bond hydrolyzable by the alkaline or enzymatic route, such as an ester, amide, thioester or thioamide bond, or cleavable by chemical or biological oxidation, such as a double or triple bond.
- 10 7. The hydrophilic polymer as claimed in any one of the preceding claims, constructed on pentaerythritol tetramercaptopropionate.
- 15 8. The hydrophilic polymer as claimed in any one of claims 1 to 6, constructed on trimethylolpropane trimercaptoacetate.
- 20 9. The hydrophilic polymer as claimed in any one of claims 1 to 6, constructed on glycol dimercaptoacetate.
10. Use of the hydrophilic polymer as claimed in one of claims 1 to 9 in compositions for detergency.
- 25 11. The hydrophilic polymer as claimed in one of claims 1 to 9, characterized in that it is crosslinked by difunctional agents to form carboxylic polymers which can be used as superabsorbants.

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(54) Title: DETERGENT BIODEGRADABLE POLYACRYLATES

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(54) Titre: POLYACRYLATES BIODEGRADABLES POUR LA DETERGENCE

(57) Abstract: The invention concerns novel biodegradable polymers consisting of a biodegradable core bound to at least two carboxylic polyacid-based branches via a bond capable of being broken by hydrolysis or by oxidation. The invention also concerns biodegradable detergent compositions containing said products.

(57) Abrégé: L'invention décrit des nouveaux polymères biodégradables constitués d'un cœur biodégradable lié à au moins deux branches à base de polyacide carboxylique par l'intermédiaire d'une liaison susceptible de se rompre par hydrolyse ou par oxydation. Elle décrit aussi les compositions détergentes biodégradables contenant ces produits.

DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

DETERGENT BIODEGRADABLE POLYACRYLATES

the specification of which

is attached hereto

was filed on 7 AUGUST 2000 as United States Application Number or PCT International Application Number PCT/FR00/02265 and (if applicable) was amended on _____

I hereby authorize our attorneys to insert the serial number assigned to this application.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 USC §119

APPLICATION NO.	COUNTRY	DAY/MONTH/YEAR FILED	PRIORITY CLAIMED
99/10433	FRANCE	12 AUGUST 1999	YES

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

PROVISIONAL APPLICATION(S) UNDER 35 U.S.C. §119(e)

APPLICATION NUMBER	FILING DATE

I hereby claim the benefit under 35 U.S.C. §120 of any United States application, or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

PRIOR U.S./PCT INTERNATIONAL APPLICATION(S) DESIGNATED FOR BENEFIT UNDER 37 U.S.C. §120

APPLICATION NO.	FILING DATE	STATUS — PATENTED, PENDING, ABANDONED

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith: I. William Millen (19,544); John L. White (17,746); Anthony J. Zelano (27,969); Alan E.J. Branigan (20,565); John R. Moses (24,983); Harry B. Shubin (32,004); Brion P. Heaney (32,542); Richard J. Traverso (30,595); John A. Sopp (33,103); Richard M. Lebovitz (37,067); John H. Thomas (33,460); Catherine M. Joyce (40,668); Nancy J. Axelrod (44,014); James T. Moore (35,619); James E. Ruland (37,432); Jennifer J. Branigan (40,921) and Robert E. McCarthy (46,044)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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